

Photolysis of O₂: Key to Chemistry of Middle Atmosphere

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August 18, 2000

As a summer student at the National Center for Atmospheric Research, my project was to make improvements to an existing photochemical model. In specific, I was to study the photolysis rate of O₂. O₂ photolysis is crucial to stratospheric ozone formation (recombination of O atoms with O₂) and is also important in climate modeling of the middle atmosphere. My work involved creating a separate code to act as a check on the existing photochemical model TUV: tropospheric ultra-violet visible. (Indeed, my code could very well act as a possible input into TUV replacing TUV's existing framework for JO₂). In doing so, this approach would also allow me to see where certain errors are in TUV. My code is meant to do a fast calculation of JO₂ in the wavelength range of 121nm – 240nm. An exact calculation would require an unnecessary amount of computer time. I achieve a fast, accurate calculation by using various parameterizations (from previous research) and algorithms that closely approximate the exact JO₂.

My method for calculating JO₂ is as follows. I split the wavelength region of interest into four distinct bands or continua: lyman-alpha, then the Schumann-Runge Continuum, followed by the Schumann-Runge Bands, and last the Herzberg Continuum. Each group was then subdivided into bins. I would find J for each bin and sum over all the bins to achieve a J for the particular band or continuum. For each band/continua I needed a solar flux at the top of the atmosphere (F_{∞}). This was provided by the Solstice website (<http://lasp.colorado.edu/solstice/solsticehome.html>) with the file containing the data named flux_coef.dat.

For the lyman-alpha band, I used Kockarts's parameterization (Kockarts, 1997), $R = \sum_{i=1}^3 a_i(e^{-b_i \times \text{NO}_2})$ where R is a function of NO_2 only. A and b are coefficients determined by fitting to exact R vs. NO_2 curve. Then $J = \int (F_{\infty}) (R) d_{\lambda}$. There is only 1 bin in this band stretching from 121.4 to 121.9 nm. A matter of importance in this band is with the third term in this parameterization, as it is not significant below about 135 km and is wrong at higher altitudes. The third term creates a sudden increase in J at these higher altitudes, leading to an abnormal profile of J . Only two terms should be used for an accurate J lyman-alpha.

There is high variability of J in the lyman-alpha band due to the variability of flux. My code presently uses solar medium. As one can see (on attached sheet), the integration from my code (using SOLSTICE's spectral data) is very close to SOLSTICE's own integration that uses a Gaussian. The lowest line is based on a parameterization from Marcel Nicolet (Nicolet 1984).

In the Schumann-Runge Continuum, I used a simple Beer-Lambert equation: $J = \int (F_{\infty}) (\sigma_{\text{O}_2}) (e^{-\sigma_{\text{O}_2} \times \text{NO}_2}) d_{\lambda}$, going from 121.9 to 175.439nm. Cross-section data came from the website <http://espsun.sapce.swri.edu/amop/buttons.html#1> and is in my code under the filename 'BRNOUT.' Here, I pre-calculated a σ_{O_2} that was weighted by the solar flux at the top of the atmosphere. More work has to be done in the future for this continuum, in regard to how it is subdivided. Currently I employ a one-bin approximation (in essence calculating J one time), but perhaps more bins would yield more accurate results.

Similar to the lyman-alpha parameterization is the method for J calculation for the Schumann-Runge Bands (175.439 – 204nm) (Kockarts 1994). For this wavelength group, $R_j = \sum_{i=1}^6 a_{2i-1}(e^{-a_{2i} \times \text{NO}_2})$, where j is 500 cm^{-1} bin. In the original formula there were 16 500 cm^{-1} bins. I cut this down to 13 by averaging adjacent bins with close R -values. I was able only to match up pairs, not combining say 4 adjacent bins into one. The J -value for each bin is found by multiplying R_j by the etf (extra-terrestrial flux). Then, the J -value for the Schumann-

Runge Band is achieved by summing all 13 bins together. There is more work to be done in this band as well, in cutting down the number of bins further. Perhaps looking at the coefficients under the sigma will allow one to throw away an exponential term.

Finally, the Herzberg Continuum (194-240 nm) is taken into account for photolysis of O_2 . Like the Schumann-Runge Continuum, a Beer-Lambert law is used. However, instead of a weighted cross-section, an exact average x-section for O_2 is calculated using Yoshino's formula for J_{O_2} valid for λ between 194-240 nm (full width of this continuum) (Yoshino, 1988). I employ a one-bin approximation for the photolysis rate, though more bins may be needed to obtain better accuracy.

In comparing my results to TUV I found that the profiles for J-total (all bands/continua) were similar (see attached printouts of my code and TUV). I discovered that in TUV, the Lyman-alpha line used all three of Kockarts's terms thus the sudden jump is seen in the graph. Ignoring the jump, the two models compare well in this wavelength region. The curve for the Schumann-Runge Bands including Herzberg Continuum for TUV is very close to that using my code. TUV's Schumann-Runge Continuum is off from my version. I do not trust either one model in this continuum, since TUV uses only two bins (2nd bin: 123-175) and my code uses just one. TUV also has problems with J for high altitudes, especially at low sun (high solar zenith angle).

If my fast JO_2 calculation is to be used in the future, many improvements are necessary. These improvements are in selecting the correct number of bins in the two continua as well as the Schumann-Runge Bands. The Schumann-Runge Bands will be much harder to improve, as it would be necessary to look at all the coefficients used in the parameterization. As for the calculation of J for Lyman-alpha, the only matter there is to ensure that only the first two terms of Kockarts's parameterization be used. I am confident of the Lyman-alpha photolysis rate found using my code for two terms. Lacking in my code are effects of scattering of radiation and

absorption by ozone. This can be fixed easily if my code is incorporated into TUV, since TUV accounts for these effects.

I would like to acknowledge the National Center for Atmospheric Research and the National Science Foundation. I also thank my mentor Dr. Sasha Madronich of the Atmospheric Chemistry Division of NCAR, as well as Dr. Dan Marsh for helping me along the way. Last, special thanks goes to the Oak Ridge Institute for Science and Education and the Dept. of Energy for funding me this summer and for allowing this great opportunity.

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